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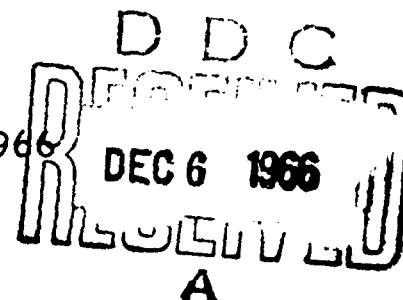
BATTERY SEPARATOR MECHANISMS--
LITERATURE SURVEY REPORT

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BATTERY SEPARATOR MECHANISMS--LITERATURE SURVEY REPORT

Prepared by:
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ABSTRACT: In order to improve the characteristics of batteries, it has become necessary to gain a greater understanding of battery separators and how they can inhibit the motion of ions and molecules. This report, based upon a three-month literature survey, reviews some of the theories invented to explain the transport of material through solutions and barriers. Included, for example, are the major fields of diffusion, electrodiffusion, irreversible thermodynamics and reaction rate theory, with specific reference to the work of Fuoss, Laity, Lamm, de Groot, Laidler and Eyring, and others. This report is intended to serve as a guide for future research.

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26 September 1966

This literature survey on the theories of mechanisms applicable to the functions of battery separators has been conducted as a part of a Battery Evaluation and Supporting Research project funded by Task RUTO 3E000/212. This project is directed toward understanding and improving the performance of the silver-zinc battery. A study of the ionic species involved in the battery reactions has been under way for some time. It is apparent that the ionic barrier (separator) used in this system is extremely critical to the successful construction of a battery. In preparation for a program expansion into a separator study, the readily available literature has been reviewed. This bibliography of pertinent literature concerning theories of separator performance is submitted as reference material for planning a separator study program.

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By direction

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INTRODUCTION

With the exception of some fairly recent technical reports from industry, the volume of literature pertaining directly to separators is quite small. And unfortunately, very few of the technical reports are concerned with the fundamental problems which must be solved. However, since the passage of ions and molecules through a separator is basically a diffusion problem, the literature has been searched for information concerning diffusion, especially diffusion through barriers, and related topics such as ionic size, hydration effects, and viscosity. During this study, some references devoted to battery separators were naturally discovered; these, and a few of the better technical reports, are also included in the bibliography.

This report may be roughly divided into two main sections, the first dealing primarily with the general aspects of diffusion and membrane transport, the theoretical explanations, and the influencing factors. The second part is devoted to items of a more specific nature, such as permselective membranes, monolayers, and specific papers of interest. This division emphasizes the two main approaches which may be followed in future research: the general versus the specific. Theoretical explanation of electrodiffusion is needed in addition to the detailed knowledge of individual systems used for commercial applications.

OBSTRUCTIONS TO THEORETICAL PROGRESS

Self-diffusion and the binary-diffusion of "ideal" liquids and gases are well known phenomena which can be analyzed by standard methods, although the careless selection of boundary and initial conditions can make this very difficult mathematically. Literature on these problems is plentiful, both in books such as Crank's Mathematics of Diffusion, Barrer's Diffusion in and through Solids and Jost's Diffusion in Solids, Liquids and Gases; and in the periodicals.⁷⁶ Consequently, only a few articles pertinent to these topics are mentioned here or included in the bibliography. The situation is quite different with respect to the diffusion of real liquids or the electrodiffusion of ions in solution. Knowledge about these systems (equations of state, etc.) is slight compared to the understanding of gases or liquids that approximate ideal behavior. This deficiency is a serious impediment to progress in these fields.

Probably the greatest obstruction is the dependence of diffusion processes upon environment. Any change in the physical or chemical nature of a diffusion system can, and frequently does, alter the results significantly. For example, this dependence automatically precludes the simple extension of dilute solution theories to more realistic concentrations, and it prohibits the study of complex systems by decomposition into simple units. Linearity does not apply except in crude approximations. Honest attempts to study real problems without simplification are few, and many existing studies applicable to dilute solutions, such as membrane potential theory, are useless at higher concentrations. Binary diffusion, the diffusion of one substance through another medium, is fairly easy to treat using Fick's law on the assumption that the diffusion constant is independent of concentration. However, the addition of a third diffusing substance seriously complicates the problem by requiring the solution of two coupled partial differential equations^{19,45,112} subject to proper initial and boundary conditions.

FACTORS IN TRANSPORT

Before continuing with a more detailed discussion of the theories, it will be best to have some conception of the many factors and mechanisms involved in diffusion and membrane problems. Incipient theories must either account for specifically, be independent (tacit inclusion) of, or neglect these factors. Unfortunately, since it appears impossible to include specifically most of these factors, the practice is often to neglect them, giving theories which at best are only applicable for very special cases. Although extensive, the following list of transport factors cannot be called complete.

1. Physical size and shape of the membrane pores and the particles, effective surface area and thickness of the membrane, etc. Many of these topics are discussed in Scheidegger;^{14B} ionic size is discussed in a review article by Stern and Amis.¹⁵⁹

2. Relative rate of adsorption on the membrane surfaces. Most surface chemistry books devote considerable space to adsorption phenomena and both Crank^{7B} and Barrer^{1B} discuss adsorption. The latter is the better reference for the physical picture (Chapter IX), particularly for cellulose membranes.

3. Relative rate of reaction of diffusate with electrode materials, with other species in the solution, or with the membrane itself. Crank discusses the mathematical aspects of the problem (Chapter 8) and Bird, Stewart and Lightfoot^{2B} include

it in their general equations and present a number of problems involving diffusion with chemical reaction.

4. Concentration differences--a few effects of:

a. Osmotic pressures.

b. Changes in the diffusion constants,⁸⁴ mobilities (especially when ions of different valence are present), adsorption rates, etc.

5. Formation of complex ions.

6. Hydration:

a. Decrease in mobility in the solution and in the membrane as hydration increases.^{131,149}

b. If a hydrated ion cannot physically pass through the membrane, energy must be supplied to remove the (ordered) water molecules.^{27,131,39}

7. Electronic charge of the ion, especially if a field is present. Jackson and Coriell⁷⁴ indicate its importance even in the absence of an imposed electric field; it is, of course, fundamental in electrodifusion.

8. Magnitude of the electric current.⁸³

9. True ion-exchange processes (generally an increase in permeability as the exchange sites are exhausted).

10. Electric field effects.

a. Electro-osmosis.^{42,183A}

b. Ionic current--magnitude and direction of ionic velocities.

11. Chemical transport by complexing with a carrier molecule or by complexing with the membrane and subsequently redissolving.^{24,3B(p.293)}

12. Proton-transfer processes ^{15B(p.57)} and similar type processes for hydroxyl ion.

13. Convection due to mechanical forces.

14. Temperature effects:

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a. As a first approximation, we may suppose the temperature dependence of the diffusion constant to be of the form $A(T)e^{-\Delta E/kT}$ as suggested by Glasstone, Laidler and Eyring.^{10B(p.522)} Experimental evidence for simple systems is given by Bowers and Wilson²⁸ and Zowleski, Eyring and Reese.¹⁷⁵

b. Convection currents from heat due to chemical reactions and resistance to current flow.

15. Time dependence of membrane parameters:

a. Physical clogging or chemical destruction.

b. Swelling and degree to which it has been "wet."¹²⁰

16. Liquid junction and phase boundary effects--barriers to flow.

17. Electrical double layers.^{183A}

18. Mass flow of solvent:

a. Effect increases with size of solvent particles²⁴ and is an aid to diffusion if both are in the same direction.

b. Viscosity of the fluid.³¹

FORCES

In a free solution we may expect three general types of forces to contribute to the movement of ions. These are the frictional forces resulting from contact between particles of different velocity and the chemical and electrical forces resulting from gradients in the concentration (or chemical potential) and the electric potential. One of the best qualitative discussions of the interplay of these forces is presented in an article by Laity⁹¹ in addition to his mathematical treatment of the same problems. A simple example of his qualitative reasoning which is simply a balancing of forces is given in the following paragraph.

Consider the steady state movement of positive ions in a bath of neutral solvent molecules through a thin "stagnant diffusion layer" to a negative (planar) electrode. At the surface of this electrode the ion concentration is zero as a result of chemical removal. There are few negative ions compared to the number of solvent molecules, and they do not contribute to the current. Consequently, they may be neglected completely. In the steady state there is no net movement of solvent molecules

and since the molecules are neutral, the forces due to friction and the concentration gradients must be equal in magnitude and opposite in direction. The force due to friction results from the movement of the positive ions through the solution and consequently this force on the molecules must be directed toward the electrode. The balancing force due to concentration gradients is in the opposite direction, implying the solute is more concentrated near the electrode surface, and the positive ions less concentrated. This yields immediately the direction of force on the ion due to its concentration gradient. It must be toward the electrode surface, and since this is also the direction of the electrical force, the frictional force must be in the opposite direction (which is known already from Newton's third law) and equal in magnitude to the sum of the other two forces.

Laity, with the aid of diagrams, applies this type of reasoning to more complex systems to obtain similar qualitative results. It is an easy and valuable way of viewing problems which should also be applicable to phenomena such as electro-osmosis and the transport of ions and molecules through membranes.

REVIEW OF THEORIES

In the following paragraphs some of the more important theories related to the transport of matter through membranes will be discussed. Their order of appearance reflects a desire to index them according to both popularity and vintage, and consequently should not serve as a basis for judgment.

A. Hydrodynamic

The extension of hydrodynamic laws--the most popular victim appears to be Poiseuille's law--to membranes is a procedure which occurs far too frequently in separator studies, as can be seen from the industrial technical reports. This extension begins with a simplified model for the membrane and the permeating substances, and the generally false hope that nothing essential has been omitted. The most common yet most unrealistic model assumes the membrane can be represented as a bundle of thin, cylindrical, chemically unreactive capillary tubes and that the permeating substance may be represented as a liquid composed of spheroidal particles. A simple application of Poiseuille's law to data on the rate of water flow through the membrane (with a known pressure gradient) determines the "pore radius." The pore radius value obtained in this fashion probably represents the actual average physical dimensions of the pores (if they exist) to within an order of magnitude and

perhaps much closer. The simplicity of both the mathematics and the experimental work makes this a valuable method for obtaining such estimates of the physical dimensions. However, the assumption, even in the most elementary cases, that one substance will pass through the membrane easier than another, based upon comparison of the pore size with the particle radius, is nonsense (even when the particle radius is larger than the measured pore radius). Some surprise is justified in elementary situations if the larger particles are transferred more rapidly than the smaller, but not in the complex cases. Whenever this phenomenon occurs, it is an indication that mechanisms other than mere physical screening are important. For this reason, size measurements may be very useful. Realization of the shortcomings of this membrane model has led to the introduction of parameters like tortuosity⁹⁸ and effective surface area which probably improve the accuracy of the results somewhat, although they cannot cover the basic faults of this approach.

Another model frequently employed assumes that the membrane can be represented as a bed of packed spheres. For discussion of the water flow through sand beds, glass bead columns and porous rocks resulting from "pressure gradients" this is a fairly realistic model, but its extension to other types of barriers and other types of driving forces (electrochemical gradients) is unjustified and can only lead to failure.

For further information on membrane models and the hydrodynamic method of analysis the best reference is The Physics of Flow through Porous Media by Scheidegger.^{14B} An example of a more detailed analysis of a specific problem is given by Goodnight, Kilkoff and Fatt.⁵⁵ More on the positive side, Solomon's work¹⁵⁴ indicates Poiseuille's law may be applied to microscopic capillaries, thus supporting its use in certain types of problems. Additional references are available in the American Institute of Chemical Engineers Journal.

B. Membrane Potential

Much of the literature on membranes is devoted to membrane potentials and related topics such as Donnan equilibrium theory. The membrane potential is the voltage across the membrane which occurs when it separates solutions of electrolytes having any concentration differences. The origin of the membrane potential is attributed to differences in the rate of diffusion of ions across the membrane which upsets the electrical neutrality of the solution.

The analysis of this potential is generally based on the Nernst equation (or very similar equations) with occasional use

of the Donnan theory. Most of the work follows closely the early efforts of Michaelis, Teorell, and Meyer and Sievers, based on the theory of liquid junction potentials. The discussion of liquid junction potentials by MacInnis^{12B} and the articles by Wyllie,^{172,173} also containing a review of the work of Marshall¹¹⁴ and Sollner,¹⁴²⁻¹⁵² are good examples of this approach. Provided the membrane potentials and chemical activities are known, the determination of mobility ratios for ions in simple systems such as NaCl solutions becomes possible. Unfortunately, in systems of more than three diffusing ions, especially if there are several (different) valence magnitudes, the equations become too complex to allow any simple determination of these ratios. There are also questions about the validity of this approach, especially in very strong solutions, and the drawback that mobilities are not determined under conditions of constant current.

The Meyer-Teorell-Sievers (M.T.S.) theory is the most popular explanation of membrane potentials, but there are other, more sophisticated methods. Kobatake,^{81,82} for example, derives expressions for the voltage and permeation rates of ions from the entropy production in the membrane. A more recent discussion of membrane potentials is given by Hills et al^{68,69} who reformulate, in terms of present concepts, the old theories of Scatchard and M.T.S. Additional references given in the bibliography are the articles by Bergsma and Staverman,²³ Helfferich,⁶¹ Meyer,¹⁰⁸ Nagasawa et al,^{115,116} Sollner et al^{149,150} and Spiegler et al.¹⁵⁶

C. Reaction Rates

There are two basic theories to be discussed in this section, both developed principally by Laidler and Eyring. These are "reaction rate" theories for the diffusion of molecules in solution and through membranes.

Laidler and Eyring's theory of liquid diffusion is based on a lattice-like structure for the liquid, with some lattices occupied by molecules and others vacant. Each molecule is assumed to occupy a small space and to interact only with its immediate neighbors.³¹ Diffusion then occurs by the jumping of a molecule to a vacant site. These sites^{10B(p.518)} are considered as potential wells separated from each other by a distance λ (considering here only one direction). Then, if the concentration at the first site is C , at the next site in the direction of diffusion it is $C + \lambda(dC/dX)$. The number of molecules moving in the direction of diffusion per sq. cm. per sec. is $v_+ = N_0 C \lambda k$, where N_0 is Avogadro's number and k is the specific rate constant for diffusion. Similarly, for the reverse motion we have $v_- = N_0 [C + \lambda(dC/dX)] \lambda k$. Consequently,

the net flow is $v = -N_0 \lambda^2 k (dC/dX)$ which requires only a few changes of units to be the familiar expression of Fick's law with $D = \lambda^2 k$. Further refinements of this are discussed in Chapter IX of The Theory of Rate Processes.^{10B} This technique is developed further by Zowlanski, Eyring and Reese,¹⁷⁵ who use it to discuss membrane permeability.

In three articles, Laidler and Schuler⁸⁶⁻⁸⁸ discuss membrane permeability and related problems. They start by assuming the solutions on each side of the membrane are highly stirred, so that the rate determining steps are adsorption and desorption at the membrane-solution interface and diffusion through the membrane. If N = the mole fraction of solute in the solution and N' = the mole fraction of the solute adsorbed on the membrane face, then the rate of adsorption is given by $v_1 = k_1 N (1 - N')$. That is, v_1 is proportional to the concentration of solute in the solution and to the number of sites available for molecules to be adsorbed on the membrane face. The rate of desorption is simply $v_{-1} = k_{-1} N'$. Using solutions to the diffusion equation by other authors, Eyring and Schuler justify the assumption that the rate of diffusion into the solid membrane is $v_2 = k_2 N'$, where k_2 is a function of the diffusion constant. Then, if the rate of entry into the solid is much greater than the rate of change of concentration of molecules on the interface, a steady state process occurs. Hence,

$$k_1 N (1 - N') - k_{-1} N' - k_2 N' = 0$$

Solving this equation for N' , the rate of entry into the membrane is found to be

$$v = k_1 k_2 N / (k_1 N + k_{-1} + k_2)$$

With this equation as a starting place, Laidler and his co-workers discuss a number of important membrane problems.

Glasstone, Laidler and Eyring^{10B}(pp.522-27) extend the "rate process" method to electrolytes, giving the following expressions for the conductance and the diffusion constant (for a single univalent electrolyte).

$$\Lambda_i = \frac{D_i Z_i F^2}{RT}$$

$$D = \frac{2RT}{F} \frac{\Lambda_+ \Lambda_-}{\Lambda_+ + \Lambda_-}$$

Some supporting experimental evidence for these equations is mentioned by these authors. These results are only applicable to "simple" electrolytes.

D. Diffusion

Use of the diffusion equation in either of its two forms, the first known widely as Fick's law, is the most common approach to analysis of the movement of material through membranes. Fick's law assumes that the rate of transfer of the diffusing substance (diffusate) through a surface of unit area is proportional to the concentration gradient; that is,

$$J = -D \frac{\partial C}{\partial X},$$

where D is the diffusion constant. A simple application of the "conservation of matter" to an infinitesimal rectangular volume element then gives the standard form of the diffusion equation for isotropic media:

$$\frac{\partial C}{\partial t} = \text{div} (D \text{ grad } C)$$

which becomes

$$\frac{\partial C}{\partial t} = D \nabla^2 C$$

if D is independent of concentration.^{7B(pp.1-5)} This form of the diffusion equation is strictly applicable only to self- and binary-diffusion situations and these must be free from the added complication of chemical reaction and electric field effects. If a diffusion system consists of $(n + 1)$ substances, there must be a diffusion equation for each species, and it must contain terms to account for the presence of the other n components. This is frequently neglected.³⁶ The resulting system of equations can be summarized as^{19,45,112,141}

$$\frac{\partial C_i}{\partial t} = \sum_{j=1}^m D_{ij} \nabla^2 C_j \quad \text{for } i = 1, 2, \dots, (n+1)$$

One of these equations, say the $(n+1)^{\text{st}}$ can be eliminated by conservation principles directly or by use of the equation of continuity, giving a system of n coupled equations. For binary diffusion, with the solute and the supporting solvent, this reduces to the familiar diffusion equation.¹⁹ Some authors prefer to express the interdependence by addition of extra terms representing the friction between molecules of different species. These terms give the equations a strong resemblance to the phenomenological relations of Irreversible Thermodynamics

(from which they probably originated). A typical example of this type of alteration is given by Meares and Ussing^{105,106} as:

$$J_a = A u_a C_a \left[- \frac{d\mu_a}{dx} + \frac{1}{A} \sum_{i=a}^k (J_i V_i g_i^a) \right].$$

Additional modification is required if chemical reaction occurs in the system. Bird, Stewart and Lightfoot^{2B} give an excellent derivation of a general diffusion equation which provides for chemical reaction and other complicating factors in Chapter 18 of their text. The more typical treatment, discussed fully in Chapter 8 of Crank^{7B} involves the simple addition of a rate term characteristic of the chemical reaction to the right side of the diffusion equation. For a first order immobilizing reaction, the equation becomes^{7B(p.124)}

$$\frac{\partial C}{\partial t} = D \nabla^2 C - kC.$$

This type of reaction may be responsible for the concentration dependence of D in some systems.³⁵ If chemical reaction occurs only at electrode surfaces, it may be treated as a boundary condition for the ordinary diffusion equation by assuming the diffusate concentration is zero at the surface.¹³⁴ The additional changes required by electrical potential gradients existing in electrolytic solutions will be discussed under "electrodiffusion" (section F).

It must be remembered that diffusion constants are functions of concentration, temperature and physical and chemical environment in general. Consequently, when the diffusion equation is applied to a system in which a membrane separates two "distinguishable" solutions, a separate equation must be applied to each of the three individual regions. The final solution is then obtained by matching the solutions for each region to the boundary conditions such as continuity of flow and concentration.^{17,140}

In connection with the diffusion equation, there are two subjects which sometimes cause confusion. The first is purely a physical problem: that of deciding whether the transfer of material is the result of diffusion or bulk permeation.¹⁶³ Unless there is a hydrostatic pressure gradient, it is fairly safe to assume the transport is by diffusion. The second concerns the basic formulation of the diffusion equation. Some authors^{1B,7B,18} assume the driving forces are concentration gradients, while others use the gradient of the chemical potential.^{44,105,138} Even assuming that the standard relation between chemical potential and activity (concentration) is valid,

D becomes a function of ⁶⁷(p.138) ✓

$$\frac{d \log a}{d \log C} .$$

Proper understanding of this problem is necessary for the study of real systems.

One of the useful features of the diffusion equation is the presence of the arbitrary parameter D, which is used to fit the same equation to very different situations. This gives the diffusion equation a certain freedom (like thermodynamics) from the many contributing factors. The diffusion constant is generally determined experimentally, and it, together with the differential equations and the boundary and initial conditions, characterize the (non-electrical) system entirely. There remains, of course, the minor problem of solving the system of equations. Ideally, however, one would like to make the diffusion equation completely determinate by evaluation of the constant from theory. Unfortunately, even partial success in this area has been limited to the diffusion of gases and simple liquid systems. The best known expression of this type results from an application of Stoke's law made by Einstein and others,⁷⁶ which gives:

$$D = RT/6\pi\eta rN .$$

Another familiar expression for the diffusion constant is given by Glasstone, Laidler and Eyring^{10B}(pp.522-5) as

$$D = \lambda^2 k ,$$

where

$$k = f(T)e^{-\epsilon_0/kT} .$$

A basic problem in this case is knowledge of the parameter λ . These expressions and several others are discussed in the review by Johnson and Bab.⁷⁶ They are primarily useful only for work with simple fluids or mixtures of such fluids. Other expressions are available for more complex solutions but they are often unreliable and difficult to evaluate.⁷¹ In Chapter X of their book, Glasstone, Laidler and Eyring^{10B} discuss diffusion in electrochemical systems and derive the diffusion constant for simple electrolytes in the presence of electric fields. Another good discussion of the diffusion of charged particles is given by Jost.^{11B}(pp.139-143)

There are four basic references on diffusion^{1B,2B,7B,11B} which--because they are invaluable to workers in the field--deserve discussion in this paper. The Mathematics of Diffusion

by Crank ⁴⁵, as the title implies, basically a mathematics book. Crank selects systems possessing initial and boundary conditions that can be easily expressed in rectangular, cylindrical or spherical coordinates and shows the detailed mathematical solution. The antithesis of this in approach is Diffusion in and through Solids, by Barrer, which uses mathematics only to explain physical problems. The last of the three "classic" texts is Diffusion in Solids, Liquids and Gases, by Jost. It covers a wider range of physical topics than either of the others and makes greater use of mathematics than Barrer's text. Transport Phenomena, by Bird, Stewart and Lightfoot, ¹¹¹ is an entirely different type of book. It is a chemical engineering text and as such it is oriented towards problems. However, it gives probably the finest derivations of the general transport equations that are available in print. Mass and energy flow, diffusion, and the interplay of these three transport mechanisms are discussed theoretically and in the solutions to hundreds of example problems, making this an extremely valuable reference.

E. Non-Electrodiffusion of Ions

The diffusion of ions in the absence of an electric field is a problem intermediate between that of diffusion of simple fluids and that of electrodiffusion. The requirements of electroneutrality and conservation of charge often allow electrolytes to be treated as non-electrolytes, although with some special privileges. Many solutions, for example, such as KCl-NaCl in water can be viewed as ternary diffusion systems, where Na^+ and K^+ move through a medium of water and chloride ions. ^{46,47,112} However, as the papers by Lifson and Jackson ⁹⁵ and Jackson and Coriell ⁷⁴ illustrate, the electrical forces of attraction and repulsion between ions or between ions and molecules (hydration) cannot be forgotten. These authors assume a lattice-like structure for the solution with an electric potential that is a periodic function of the space coordinates as a consequence of the structure. This solution model, which is basically a perturbation of the crystal type structure (similar to Laidler's model) implies too strong an influence for the electrical forces. The results, however, are interesting and should be useful qualitatively. As a consequence of the structure, diffusing ions are subjected to a periodic potential which strongly affects the observed diffusion constant. Lifson and Jackson, using the method of Pontyagin et al, conclude, for one dimensional problems, that the diffusion constant is always less than it would be if the potential did not exist. Using a different, but very interesting, technique, Jackson and Coriell arrive at the same conclusion for the three dimensional case. They also find, among other conclusions of interest, that the diffusion constant is greater for particles moving through potential maxima than through potential minima; this is

explained qualitatively by saying the particle is less likely to be trapped.

F. Electrodifffusion

The problem of electrodifffusion--the diffusion of ions in an electric field--has been approached in many different ways, some of which are reviewed here. The selection has been made on the basis of usage and possible merit.

One of the earliest papers of note in this field was written by H. J. S. Sand³⁴ and published in 1901. In this paper electrodifffusion is treated as "ordinary diffusion" under the assumption that the changes of concentration are neutralized by the diffusion that takes place according to Fick's law, which is not affected by the passage of current through the liquid. The electric field effects are then included as boundary conditions.

A frequent assumption in many types of diffusion problems is that the molecules or ions reach a steady velocity (as in the derivation of Stoke-Einstein relation for D) due to a balance between the driving forces and a resistive force which is generally assumed to be proportional to the velocity. Consequently, with the neglect of the dv/dt term, the equation of motion may be easily solved, giving the velocity proportional to the driving force. From here it is only a short step to an expression like $J = Et/zFR$, where J is the rate of diffusion through a membrane.⁸⁰

The Nernst equation, either directly or in one of its modified forms (Henderson equation, Nernst-Planck equation, etc.), is frequently applied to electrodifffusion problems. One example of this (mentioned earlier) is its use in determining ionic mobilities in membranes from the membrane potential. Another example, which is worth mention on its own merits, is from a paper by Davies.³⁹ He found experimentally that the rate at which a salt passes through a phase boundary between liquids is proportional to $(k_1C_1 - k_2C_2)$, where k_1 and k_2 are constants and C_1 and C_2 are the concentrations on the two sides of the boundary. The basic equation used is a highly modified Nernst equation having the form:

$$v = -u \frac{dE}{dx} - \frac{u}{C_1} \frac{RT}{F} \frac{dC}{dx} - \frac{u}{F} \frac{d\psi^0}{dx}$$

where v is the velocity and u the mobility of the ion in question. An interesting result is that an interface 10 Å thick can decrease the ionic mobility by a factor of (say) 10^6 .

Many authors use, instead of the concentration gradients, the gradient of the chemical potential. This may be carried a further step with the use of the electrochemical potential,^{44,105} which includes both the usual chemical potential term and a term representing the electric potential. That is,⁴⁴

$$d\mu_i^e = (d\mu_i^e)_{d\varphi=0} + Z_i^f F d\varphi$$

where the first term on the right is the non-electrical part and φ is the electric potential. It might appear in the diffusion equation as

$$J_i = -D\nabla\mu_i.$$

This is quite similar, when expanded, to the Nernst equation shown above, and when put in the form of the second diffusion equation, to the expressions used by Bak and Kauman¹⁸ in their treatment of electrodiffusion. A continuation of the work of Bak and Kauman, beginning with a correction of an error in the integrated equations, is given by Scholten and Mysels.¹³⁷

The field of electroanalytic chemistry contains some literature which is applicable to electrodiffusion problems of interest. The articles included here for reference are by Bowers et al,^{28,29} Delahay et al,^{25,40,41} and by Markowitz and Elving.¹⁰¹ Of particular interest is a paper by Bowers and Wilson²⁸ and a paper covering similar material by Delahay and Mamantow.⁴¹ Bowers and Wilson discuss a situation in which the electrode being studied is wrapped tightly with cellophane. They make the fundamental assumption that the rate controlling step is diffusion through the membrane. Then, the concentration of the electrolyte between the electrode and the cellophane is zero as a result of rapid chemical removal, and is equal to "C" at all other parts of the solution exterior to the membrane. Since

$$J = -D \frac{\partial C}{\partial X}$$

in the membrane and $i = JnFA$, when a steady state is achieved, the expression (used as a boundary condition)

$$i = nFDA \left(\frac{\partial C}{\partial X} \right)_{X=0}$$

is valid. In this case, the approximation $(\partial C / \partial X)_{X=0} = C/l$ is probably quite accurate. If the factor A/l is known, the procedure gives a fairly easy method for evaluation of D for the current carrying ions in the membrane. This same type of

procedure should be applicable to stirred solutions (although¹³⁵ stirring may alter results) separated by a membrane, the only change being the replacement of C by ΔC . Additionally, Bowers and Wilson discuss the effect of area on current, the evaluation of diffusion constants by the rate of approach to steady state, and by a small-time approximation (not requiring knowledge of A/l), the determination of the amount of cadmium adsorbed by the cellophane from differences between predicted and experimental results, and the temperature dependence of the diffusion constant.

Most of the present fundamental research in the field of electrodiffusion is divided between three different types of approaches. These three are well represented by the work of:

1. Fuoss: a hydrodynamic attack based on the Navier-Stokes^{183A} equation, ionic size and shape, etc.⁵⁰

2. Laity: whose work^{89,90,91} is an application of the irreversible thermodynamics of Onsager, de Groot and others (about which more will be said), and

3. Lamm: who develops the concept of friction coefficients and uses them to modify the diffusion equation. There is also some appeal to irreversible thermodynamics.^{92,93,94}

The omission of a detailed review of these theories in this paper is not an indication that they are insignificant; the reverse is actually true. Any individual doing research on electrodiffusion problems should at least be familiar with them. Unluckily, the subject of membranes is rarely introduced in this work, although Duncan's paper⁴⁴ is an exception; electrodiffusion has enough difficulties of its own. Some other researchers utilizing these approaches are Meares and Ussing,^{105,106} Hills et al,^{68,69} Dunlop,⁴⁷ Dunlop and Gosting,⁴⁶ and Miller.¹¹²

G. Statistical Mechanics

As with the current theories of electrodiffusion, little can be said here on the application of Statistical Mechanics applied to diffusion and membrane transport problems. The theory, as might be suspected, is far better developed for gases than for even the simplest liquids. The literature on this subject is somewhat meager, although activity is, apparently, increasing. Some references in the field which provide helpful bibliographies in addition to useful information are the books by Cox^{6B} and Prigogine^{13B} and the paper by Bearman.²² The first of these, Statistical Mechanics of Irreversible Change by R. T. Cox, is an excellent little book which devotes several

chapters to the discussion of Brownian motion and transport phenomena. The second, a recent monograph entitled "Non-Equilibrium Statistical Mechanics" by Prigogine, takes the more modern approach of irreversible thermodynamics. The paper by R. J. Bearman examines, from the standpoint of statistical mechanics, the equation of Eyring, Hartly and Crank, and/or Gordon, with respect to the concentration dependence of the diffusion constant in lipid solution. It gives a good picture of the state of development of this mode of analysis. Although statistical mechanics is a comparatively unpopular approach as a result of the training necessary and the mathematical barriers to rapid progress, it will probably be much more important in the future as a result of the desire to link macroscopic phenomena with microscopic behavior.

H. Irreversible Thermodynamics

Irreversible thermodynamics in the form usually applied to diffusion and electrodiffusion is discussed in the famous book by de Groot^{8B} and in the more recent work by de Groot and Mazur.^{9B} Another recent and very sophisticated discussion which is slanted toward statistical mechanics is available in the monograph by Prigogine.^{13B} Applications of this subject to practical diffusion problems are given in references mentioned in the last paragraph of the discussion of electrodiffusion (section F).

The expression

$$J_i = \sum_{j=1}^n L_{ij} X_j ,$$

where the flows J_i are linearly related to the forces X_j and the sum is over all the species, is representative of the equations found in this formulation of flow problems. The "phenomenological coefficients" L_{ij} are symmetric; that is, $L_{ij} = L_{ji}$. These are known as the Onsager reciprocity relations.¹¹² In addition to being linear (and integral), equations of this form place no unwarranted emphasis on a limited number of flows (an advantage of Lagrange Multipliers) and they are readily susceptible to treatment by matrix methods.⁴⁴

The linear equations are not restricted to flow rates alone. For example, Laity uses the following expression for the gradient of the electrochemical potential:

$$-\nabla \mu_i = \sum_k r_{ik} X_k (v_i - v_k)$$

where the $r_{ik} (= r_{ki})$ are friction coefficients and the v_i are

velocities. The rate of entropy production inside systems undergoing dissipative processes is given by Miller¹¹² and similarly by de Groot⁸⁸ as

$$\dot{A}S = \sum_i J_i X_i .$$

The existence of these linear relations seems to imply that irreversible thermodynamics is applicable only to steady state processes. This contention is supported by the absence of a time factor in the equations and also the proportionality between velocities and forces which is reminiscent of results of other steady state approximations. Consequently, this theory cannot be applied to analyze the transient behavior of systems. This should not, however, seriously restrict its use in the study of battery type problems in which currents often exist for relatively long periods of time.

RESTRICTED PROBLEMS

This completes the discussion of the theoretical approaches to membrane behavior and transport problems; it certainly does not include all the methods of analysis, but it does cover the main categories. The remainder of the paper is devoted to more specific topics, some theoretical and others experimental.

I. Selective Permeability

One such problem which certainly deserves study (theoretical and experimental) is the determination of the mechanisms which allow a membrane to pass some ions or molecules, while it partially or completely restricts the motion of others. It is a problem which must be studied for each individual membrane and each solution (even if only the concentrations are different). Evidence for this last statement is plentiful. For instance, Sollner¹⁴⁵⁻¹⁵² describes membranes which are permselective--they inhibit completely either the motion of all cations or all anions. However, Kressman and Tye⁸⁴ discuss membranes of this type but state they are completely selective only in certain concentration regions. Size restrictions occur in the classic osmotic pressure and Donnan equilibrium experiments, but it is one of the least important factors in function of the separator for the silver oxide-zinc battery. This cellophane separator apparently restricts the motion of silver ions by reducing them to silver metal.^{178R,181R} Evidently, the question of mechanism is not an easy one, and it is not surprising that such studies are difficult to find in the literature. Only in a few areas are the mechanisms understood or else receiving proper study. These areas include the sieve type

membrane which functions only by size exclusion; the permselective membranes whose basic mechanism is well known, and the biological membranes which are receiving intensive study. For the large remainder, comparatively little is known. One point seems clear, however; an adequate study of the inhibiting mechanisms of a particular membrane cannot be made without knowledge of the exact chemical identity of the diffusing particles. Judging from discussions with other people engaged in battery research, there seems to be considerable confusion, at least with respect to the silver-zinc battery, as to which components actually move, or can move through the cellophane separators. There is additional confusion about the chemical identity of these components in solution. Some of these obscure points could be removed by simple experiments. For example, without knowing the exact chemical identity, an estimate of the potassium mobility should be possible by radioactive labeling of one portion of the solution. This is independent of the fraction of current carried by potassium because ordinary diffusion will occur. Whatever the choice of the isotope, it must emit gamma rays, since α and β particles are stopped by the solution and are consequently undetectable. For potassium, a usable isotope might be K^{40} which emits β^+ and β^- particles and a gamma ray, with a half life of 1.4×10^9 years. Other studies of this type using Ag^{110} and Zn^{65} have been performed by Palagyi¹²²⁻¹²⁵ apparently without deleterious side effects, so that the technique can probably be applied to the other components.

J. Boundary Barriers

There exist, in addition to the conventional membranes and separators, many other barriers to the flow of material such as liquid junctions, lipoid membranes, and in general any region (or boundary) in which there is a rapid change in physical or chemical properties. Lipoid, or lipid membranes, are of interest to biologists and will be discussed in another place.

Many older references such as MacInnis^{12B} discuss liquid junctions and liquid junction potentials, although they contain no satisfactory treatment of diffusion through these junctions. However, a recent article by Rosano, Duby and Schulman¹³¹ studies the flux of salt and water through non-aqueous liquid membranes in a simple yet interesting way based upon the use of partition coefficients and the conservation of matter during steady state flows. Here as in many other studies the rate controlling step is assumed to be diffusion through the interface. In addition, activation energies for diffusion through the interface are computed, and the effects of hydration are discussed. A far more rigorous mathematical treatment of diffusion through (or across) interfaces is given by Scott et al¹⁴⁰ and Auer and Murbach.¹⁷

The subject of monolayers and natural membranes is treated nicely in a recent article by M. Blank;²⁷ it deserves to be reviewed here in some detail.

The use of Fick's law in monolayer studies is severely questioned by Blank on the grounds that unavoidable fluctuations in the thickness cause variations in the diffusion constant D . These same fluctuations in the thickness or density explain why a monolayer is more permeable than a solid, even though the state of aggregation of the molecules is much the same. The permeability is governed by the instantaneous arrangement, not by the average. Molecular jumps in the permeation process seem to be an all or none affair, so that for small thicknesses such as monolayers a strong dependence on thickness should be expected. However, with ordinary membranes the number of jumps is large enough so that the thickness variations are not important, making D constant over the surface and Fick's law applicable.

Blank mentions that the effect of hydration may be viewed in two ways. One viewpoint is that the rate of migration across the interface or boundary is retarded by the presence of the extra step involved in dehydration. The other is that the rate is decreased by the presence of the potential barrier presented in the dehydration process. Blank also recommends the use of partition coefficients in the analysis of monolayers and liquid membranes (see Rosanano et al¹³¹).

The permeation of lipid monolayers is either by dissolving or by passage through channels (pores), depending upon the solubility of the permeate in the lipid material. The assumption that membrane characteristics can be approximated by monolayer properties has led to a model of a homogeneous (lipid) membrane having functional, or transient, pores. This eliminates the need for a complicated mosaic model having both lipid and pore regions for some membranes. Finally, Blank mentions that the presence of inert substances such as water can affect the permeability of monolayers to gases (causing a net decrease).

K. Transport Number

Kressman and Tye⁸⁴ studied the concentration dependence of the transport number for current carrying ions passing through a permaselective membrane. The startling nature of their conclusions makes them worthy of further discussion. Kressman and Tye assume that under perfect conditions there is only one current carrying ion which can pass through the membrane and that its true transport number t is a monotonic decreasing function $f(C) = f'(\bar{C})$ of concentration. The symbols C and \bar{C} refer to the concentrations of the electrolyte in the solution and in

the membrane respectively. The subscript D refers to the portion of the system donating the ion to the membrane, and the subscript R refers to the part of the system receiving the ion from the membrane and the D side. As an illustration of their reasoning, consider the case where $C_D < C_R$. This implies $\bar{C}_D < \bar{C}_R$ and $f'(\bar{C}_D) > f'(\bar{C}_R)$. With a current passing through the membrane, the change in concentration of electrolyte in one sq. cm. of the membrane per sec is given by

$$i[f'(\bar{C}_D) - f'(\bar{C}_R)]/F$$

with $i > 0$. The inequalities imply the change must be an increase; and furthermore, this increase only ceases when C_D has become equal to C_R , at which point steady state prevails. Hence, in the steady state the transport number of the ion can depend only upon the concentration of the receiving side. This is a marked contradiction to the common assumption that the current density is proportional to the concentration gradient across the membrane.²⁸ Further variations of the problem are examined by Kressman and Tye with similar conclusions; the transport number depends either upon C_D or C_R alone or in some instances upon the concentration value C_M , for which t is a minimum (in this case the addition of the term $K'\bar{C}$ to $f'(\bar{C})$ allows t to have a minimum without contradiction). Experimental evidence is included in their paper, but more work should certainly be conducted along these lines.

L. Membrane Mechanism

The subject of permaselective or ion-selective (cation or anion) membranes has been broached in several places, but without explanation of exactly what they are or how they function. The identifying feature of this class of membranes is their ability to restrict the flow of cations (or anions) without causing excessive decrease in the mobility of the other species. This action is accomplished by the presence of fixed charges within the pores of the membrane. Positive (or negative) charges firmly anchored within the membrane will repel the positive (or negative) ions in the solution, thus blocking their movement through the pores. On the other hand, the negative (or positive) ions in the solution are attracted by the fixed positive (or negative) charges, and despite a tendency for them to become trapped, they are able to travel through the pores.¹⁴²⁻¹⁵²

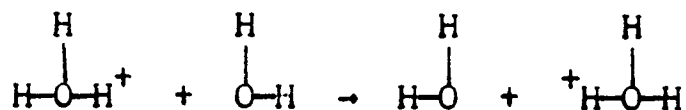
There are several possible ways to account for the fixed charges in the membrane. Sollner, for example, assumes the membranes contain molecules which can become oriented so that strong polar ends are projecting into a channel. Another possible mechanism is the preferential adsorption of ions on

the membrane--and hence on the pore--surfaces. Of note here is the tendency for ions in solution to attach themselves to radicals in the membrane with which they would react strongly if the radicals were themselves free.

Industrial uses in fields like electrodialysis^{15B,70} were easily found for ion-selective membranes, which may account for the abundance of literature material devoted to them. Some of the material, such as the work of Sollner and Gregor^{142-152, 54-57, 117-119, 52} is included in the bibliography for this report; however, this represents only a small portion of the available reports. Further information is available in journals such as J. Phys. Chem., or may be located through use of the Chem. Abstracts. Permaselective membranes are often listed in these references under the name of "ion-exchange membranes" so that some confusion may occur. The literature on true "ion-exchange membranes," which function by the actual exchange of ions between the solution and the membrane, is also very plentiful and easy to locate if information on them is required.

M. Charge Transfer

"Diffusion and Membrane Technology" by Tuwiner^{15B} presents a fair survey of the various fields of activity, both scientific and industrial, in problems relating to diffusion. One of the topics discussed by Tuwiner^{15B}(p.57) and to a far greater extent by Glasstone, Laidler and Eyring^{10B}(pp.559-575) is the abnormal mobility of the hydronium ion (and others) in hydroxylic solvents. These ions have extremely high mobilities which are attributed to transfer reactions between the ion and the solvent in the direction of the diffusion. Typical of this type of process is the reaction between water and the hydronium ion which is represented as:



direction of diffusion →

Similar mechanisms will certainly enhance the movement of some ions through the pores of membranes and perhaps in a few cases where the transport does not occur through physical holes.

N. Biological Problems

Throughout the body of an animal, from the surface skin to the cell walls, the phenomenon of membrane transport is intimately connected with respiration, reproduction, metabolism, and

the other life processes. There is ample justification for the deep interest biologists have in membranes, and it is not surprising to learn that they have contributed, and are still contributing, much of the important research in this field. Advance in biological research is hindered by the complexity of and insufficient knowledge about living organisms, and often by the necessity for experimental conditions closely approximating the real environment. However, some simplifications may result from the absence of large electric potentials and by the presence of large particles (cells, molecules or ions) which are excluded from many membranes by physical size alone. There are, of course, some problems studied by scientists in the biological fields that are not seriously examined by other investigators; an important example of this is Donnan equilibrium. As the name implies, this is an equilibrium situation; it occurs in the simplest form when a membrane separates two solutions having a common ion free and one of which contains an ion too large for passage through the membrane pores. The Donnan Theory gives a final expression for the equilibrium concentration. An elementary discussion of this is available in the text by Clark.^{4B(p.151)} Far more advanced treatments and references to additional literature are given in the articles by Hill.^{65,66}

Many biological membranes, cell walls, for example, are composed of lipid materials. These fat-like substances may well pass particles by a mechanism generally not considered for the more solid, inanimate membranes. Early studies, for example, showed that the permeability of lipid membranes to many chemicals increased with their solubility in the lipid substance. Further studies, however, have indicated the existence of pores in these membranes.²⁴ Another possibility is the combination of the diffusate with a "carrier" in the membrane. Biologists have, however, been forced beyond consideration of these elementary (basically physical) mechanisms. More imaginative chemical schemes such as the sodium, or redox pump, have been advanced to help explain the occurrence of "active transport." This term, which will presumably disappear as understanding increases, is used to designate situations in which the flux predicted by consideration of chemical and electrical gradients is vastly different in magnitude and often direction in experimental situations. For instance, experiments²⁴ on frog skins indicate they are able to take in Na^+ from the environment against concentration gradients as great as 1000:1. Furthermore, the transfer is completely specific with respect to sodium; there is no potassium or calcium transfer even though the electrochemical gradients favor such motion. Experiments also indicate that the chloride ion transport is "passive," and that the membrane potential developed is a direct function of the sodium flux. Other instances of similar phenomena are mentioned by Hartley.⁶⁰

Only a few biologically oriented articles have been reviewed for this report, and most of these come from the 1956 "Discussions of the Faraday Society," Vol. 21. Much more material is available in the biological literature, especially in the physiology journals, and if a new literature survey is desired in the near future, this is where it should begin.

O. Measurements

The subject of measurements and measurement techniques is important in any field of science. This is particularly true in the study of diffusion due to the difficulties in obtaining respectable, if not very accurate, results, and the confusion resulting from improper conceptions about the measured quantities. The misconceptions concerning diffusion constants and the effects of changing from one frame of reference to another can be removed by consulting the reference books on diffusion. Crank^{7B} devotes an entire chapter to "The Definition and Measurement of Diffusion Coefficients," while Bird, Stewart and Lightfoot^{2B} emphasize throughout their work the differences between various types of diffusion constants. The formulation of the diffusion equation determines the type of diffusion constant; proper measurements must then be made for D to be a meaningful quantity. The proper definition of the diffusion constant is not the only source of confusion and error. Duncan⁴⁴ discusses the thermodynamic definitions of membrane electromotive forces and of flows of electrolytic solutes. Irani and Adanson⁷³ study the thermodynamic complications in the testing of existing diffusion theories.

General discussions of measurement techniques are available in the review article by Johnson and Bab⁷⁶ and also in Chapter 3 of Tuwiler.^{15B} These references, if combined, will give a fair picture of the methods available, but they are short on details. Experimental determination of factors such as porosity, pore size, and other quantities important to the pressure flow of fluids through porous media is discussed by Scheidegger. For measurements on diffusion there are several optical techniques based on the refractive index gradients, and interference patterns resulting from concentration differences. These methods are extremely valuable because they permit non-destructive measurements to be made on diffusion systems. More detailed information on these optical techniques is available in articles by Dunlop and Gosting,⁴⁵ Kim, Patel and Kegles,⁷⁹ O'Brien and Rosenfield,¹²¹ Bryngdahl and Ljunggren,³² Creeth and Gosting,³⁶ and Creeth.³⁷

Additional references on measurement techniques used in specific experiments are, of course, available in many of the articles listed in the bibliography. The accompanying titles

should provide some guidance in the selection of articles for the purpose.

CONCLUDING REMARKS

The last section on measurement techniques concludes the discussion of the literature that was reviewed for the separator study. All of the articles studied for this report are included in the accompanying bibliography, but not all of them have been mentioned here in previous discussions. Additionally, by aiming for a broad coverage with concentration in the more important areas of research, a large amount of literature has been neglected. A fair number of these articles can be found fairly quickly, if necessary, because they belong to specific areas that for one reason or another were purposely ignored. For these topics, hopefully all included in the following list, there are many unlisted articles available in the major chemical and physical chemical journals.

1. Permaselective membranes (best source, probably Journal of Physical Chemistry).
2. Gaseous diffusion (Journal of Physical Chemistry, Journal of Chemical Physics, and standard diffusion texts).
3. Electroanalytic chemistry (including topics such as potentiometry, voltametry, etc.), Journal of Electroanalytical Chemistry.
4. Chemical engineering articles concerning diffusion such as those which are generously included in the American Institute of Chemical Engineers Journal.
5. Diffusion time lag studies (Journal of Physical Chemistry).
6. Diffusion of non-electrolytes (Journal of Physical Chemistry, Transactions of the Faraday Society). Furthermore, neither the biological journals nor the foreign language publications have been reviewed. There is ample material for a continuation of the literature survey.

Before concluding the report, I should like to present two personal ideas which might be worthy of further consideration; both directly concern the silver oxide-zinc battery and its cellophane separator.

One of the goals of separator research is to decrease the internal impedance of batteries, especially those designed for

high current operations. Cellophane, which is the most successful known separator material for AgO-Zn batteries, apparently owes its effectiveness to chemical reaction--its ability to reduce silver ions to neutral molecules.^{178R,181R} Hence, a possible means for increasing the permeability of the cellophane to the current carriers without destroying its effectiveness as a separator is by increasing the size of the pores. Craig and Konigsburg³⁴ found that cellophane would not return to its original size after being stretched; and by their estimation a 20% increase in pore size could be produced. Their experiments showed the time required for 50% of one diffusate (ribonuclease) to pass through the membrane could be reduced from 6.6 hours to 0.9 hour. Unfortunately, only high molecular weight organic substances were used in the experiments. Since the physical stretching decreases both the thickness and the density per unit area, it may be necessary to use an additional layer of cellophane to provide the same effectiveness as a separator. This addition will decrease the permeability of the separator, but Poiseuille's law--although not applicable to flux of material through cellophane--indicates that there should still be a net gain in permeability. The actual dependence of the flow rate upon thickness and pore size should be (at least) somewhat similar to the (pore radius)⁴/length dependence predicted by Poiseuille's law. That is, the size of the physical openings should be far more important than the thickness for changing the permeability.

Blocking the movement of silver ions is ostensibly the major function of the separator in the AgO-Zn battery. Although this is accomplished effectively by cellophane, it is desirable to have a separator that degrades less rapidly in concentrated KOH solutions. Many of the attempts to develop new membranes resistant to chemical attack are centered around modifying cellophane to reduce the degradation, or trying other materials which are chemically similar to cellophane. As an alternate procedure, it might be possible to introduce, either into the KOH solution or between the separators, a chemical substance which will either combine with the silver ion complex to change the sign (and probably magnitude) of its valence, or to tie up the silver ion complex so that it is unable to pass through the separator.

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APPENDIX I

List of Symbols

1. A surface area
2. a activity coefficient
3. C concentration
4. D diffusion coefficient (constant)
5. D_{ij} diffusion coefficient in an n-component system
6. E electric field
7. F Faraday's constant
8. $f(C)$ concentration dependence of the transport number in free solution
9. $f'(\bar{C})$ concentration dependence of the transport number in the membrane
10. g_a^i frictional force between the i th and the a th component
11. i electric current
12. J flux of diffusate per unit area per second
13. K' proportionality constant
14. k rate constant or specific rate constant
15. L_{ij} phenomenological coefficient
16. l membrane thickness
17. N_0 Avogadro's number
18. N mole fraction
19. N' mole fraction on the membrane surface
20. n number of moles
21. R gas constant

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- 22. r particle radius
- 23. r_{ij} friction coefficient
- 24. \dot{S} rate of production of entropy per second
- 25. T temperature
- 26. t time
- 27. t_i transport number
- 28. u mobility
- 29. V_i molar volume
- 30. v_i velocity of the particles of the i th species
- 31. X_j j th force
- 32. X distance coordinant
- 33. Z_i valence (number of electron charges)
- 34. η viscosity
- 35. Λ conductance
- 36. λ distance between potential minima
- 37. μ_i chemical potential
- 38. φ electric potential
- 39. ∇^2 the Laplacian

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